Solution chemistry of cubic and orthorhombic tricalcium aluminate hydration

Supporting information for:

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Rupert J. Myers [1,2,*], Guoqing Geng [1,a], Erich D. Rodriguez [3,4,b], Priscila da Rosa [3,c], Ana Paula Kirchheim [3,d], Paulo J. M. Monteiro [1,e]

[1] Department of Civil and Environmental Engineering, University of California, Berkeley, California, United States

[2] Yale School of Forestry & Environmental Studies, Yale University, New Haven, Connecticut, United States

[3] Department of Civil Engineering, Universidade Federal do Rio Grande do Sul (UFRGS), Porto Alegre, RS, Brazil

[4] Department of Civil Engineering, IMED, Passo Fundo, RS, Brazil

* Corresponding author. Email: rupert.myers@gmail.com, [a] guoqinggeng1989@gmail.com, [b] erich.rodriguez@imed.edu.br, [c] priscila.rosa@ufrgs.br, [d] anapaula.k@ufrgs.br, [e] monteiro@berkeley.edu.

Appendix A

X-ray fluorescence

X-ray fluorescence (XRF) measurements were performed on a Philips PW2400 Wavelength-Dispersive XRF machine. The estimated absolute error per $Na_{2x}Ca_{3-x}Al_2O_6$ unit is $\leq\pm0.09$ mol Ca, $\leq\pm0.01$ mol Na and $\leq\pm0.02$ mol Al.

X-ray diffraction

X-ray diffractograms measured for the solid precursors used here are shown in Figure A1.

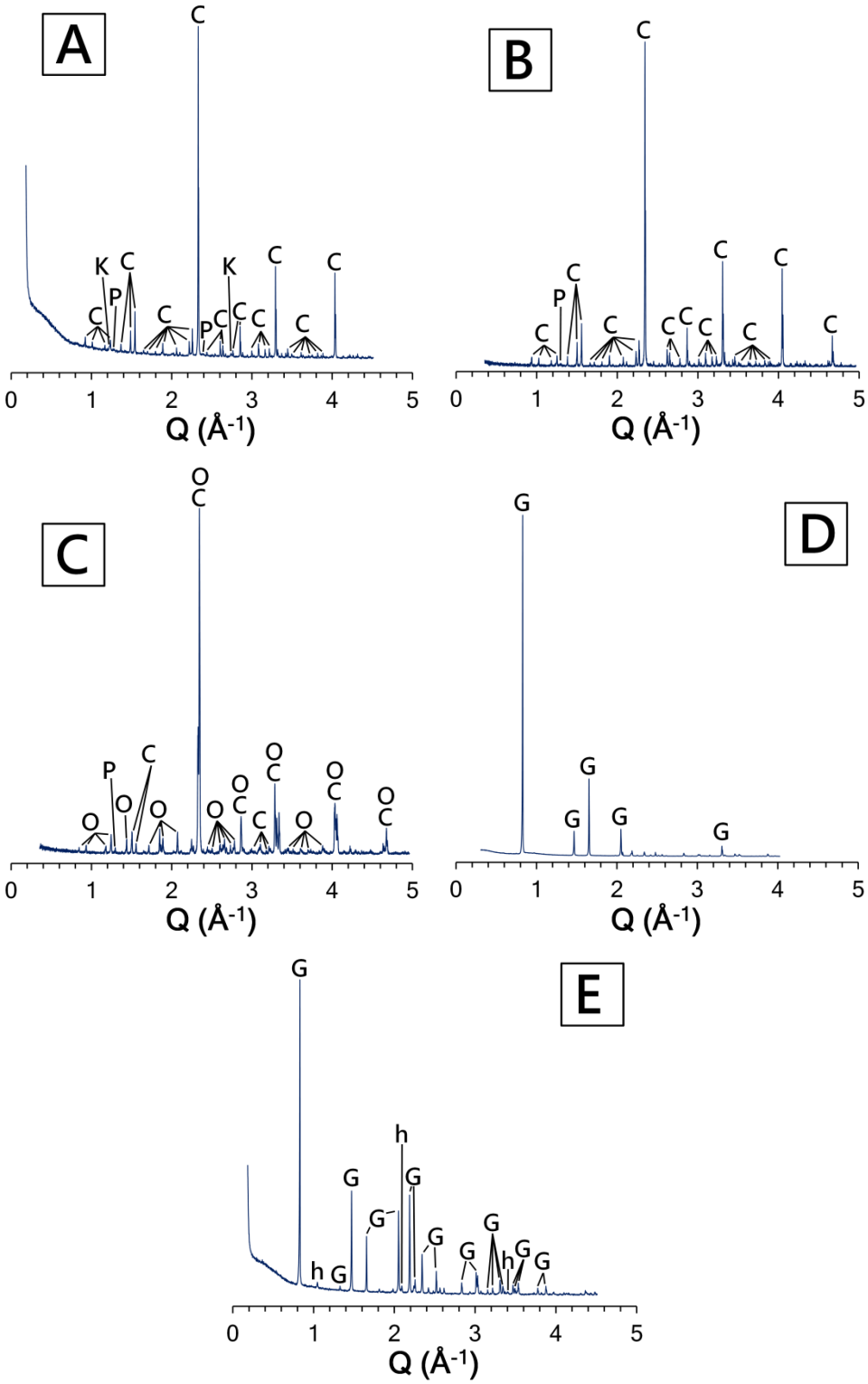

Figure A1. X-ray diffractograms of (A) cub-C_3A_1, (B) cub-C_3A_2, (C) orth-C_3A_2, (D) gypsum_1, and (E) gypsum_2. C = cubic C_3A (PDF# 01-070-0839), O = orth-C_3A (PDF# 01-070-0859), K = katoite (PDF# 00-024-0217), P = portlandite (PDF# 01-072-0156), G = gypsum (PDF# 01-070-0982) and h = hemihydrate (PDF# 01-081-1848).

Thermogravimetric analysis

The results from thermogravimetric analysis (TGA) of the precursor solids, performed on a Hitachi STA7300 operated at a heating rate of 20°C/minute up to 1000°C under an $N_{2\,(g)}$ atmosphere, are shown in Figure A2.

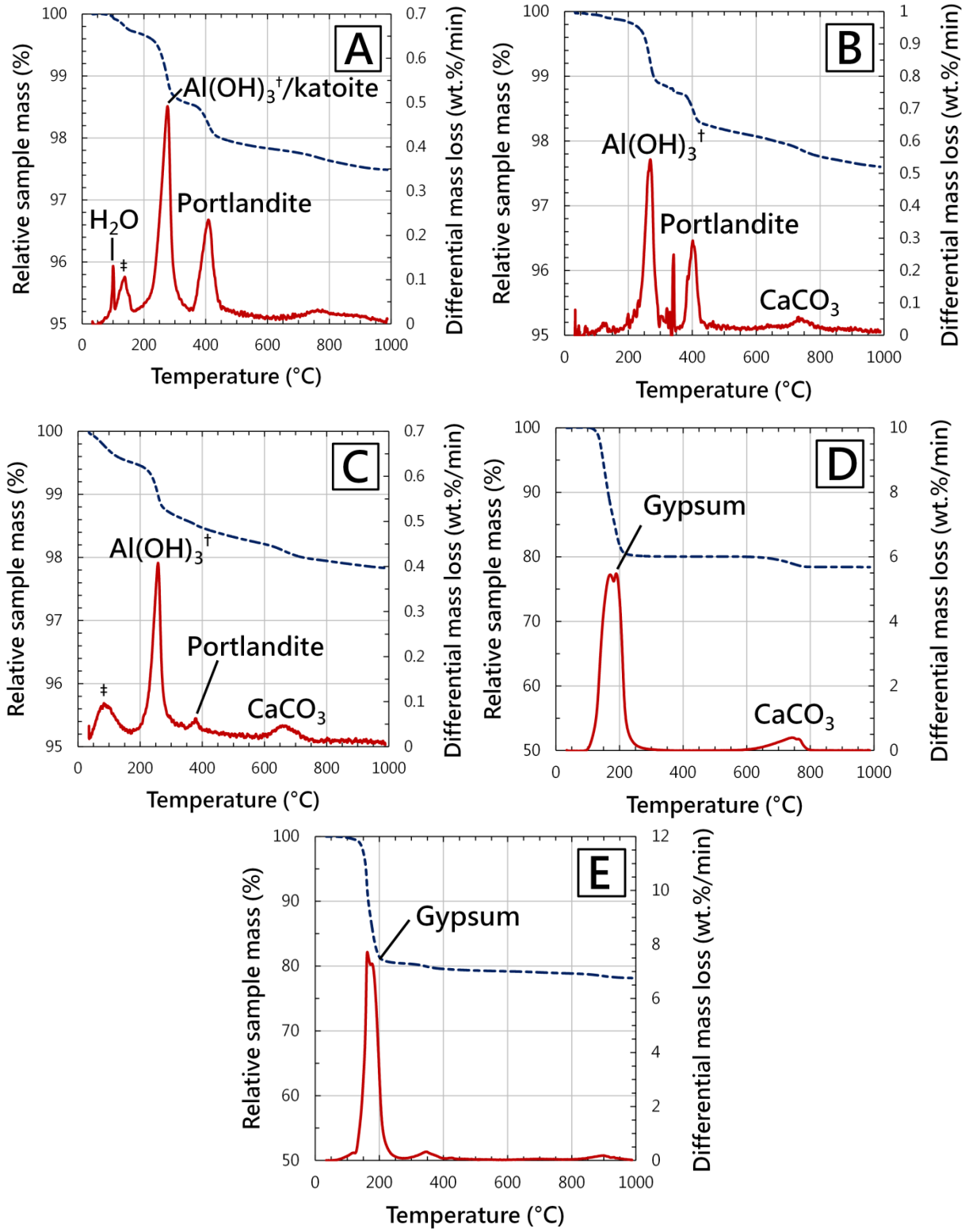

Figure A2. TGA of (A) cub-C_3A_1, (B) cub-C_3A_2, (C) orth-C_3A_2, (D) gypsum_1, and (E) gypsum_2. The labels † and ‡ indicate that the $Al(OH)_3$ is amorphous by conventional XRD and mass loss from water in poorly crystalline calcium aluminate hydrates, respectively. Minute is abbreviated as min.

Particle size distribution

Particle size distributions for the solid precursors used here are shown in Figure A3.

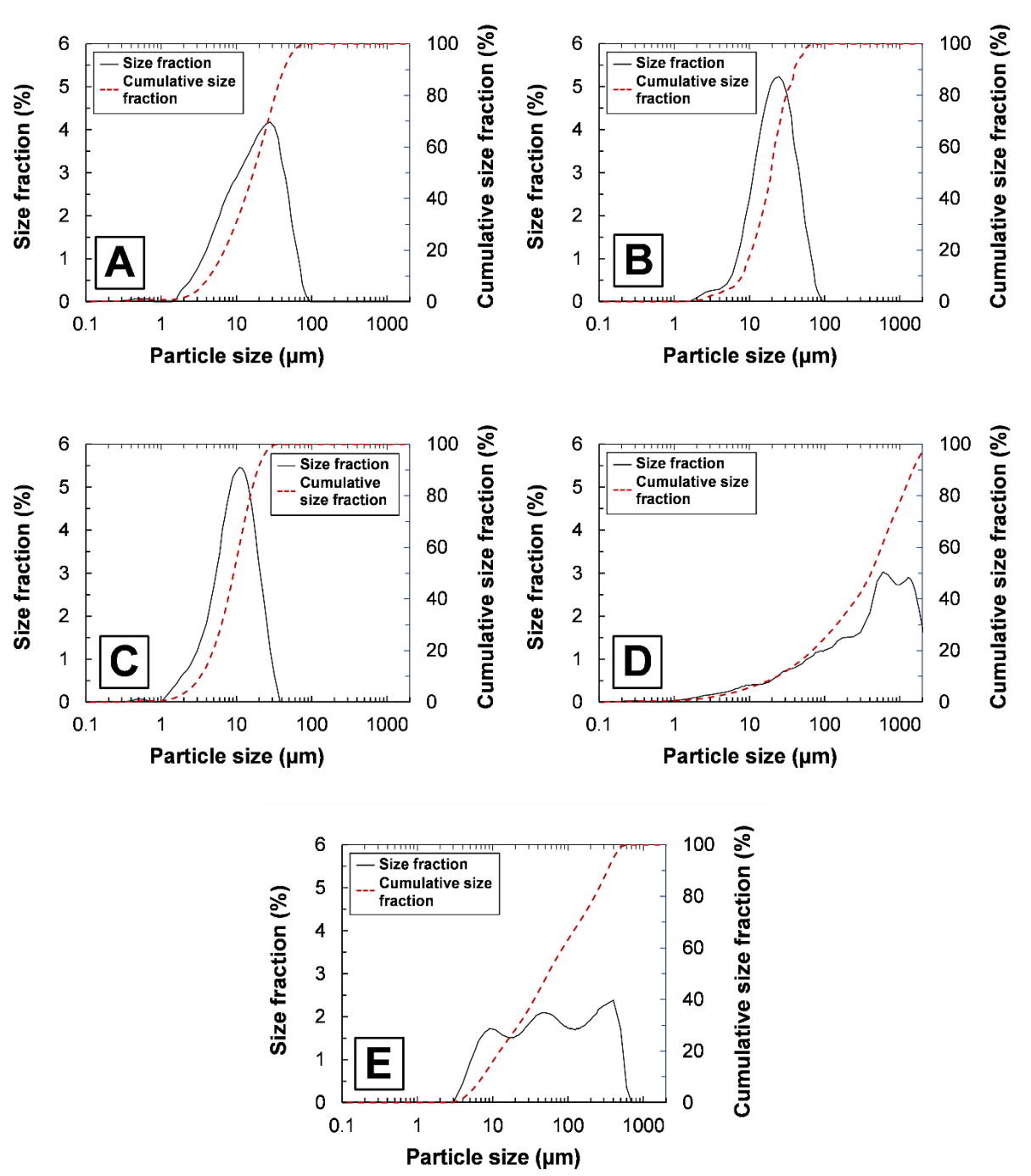

Figure A3. Particle size distributions of (A) cub-C_3A_1, (B) cub-C_3A_2, (C) orth-C_3A_2, (D) gypsum_1, and (E) gypsum_2.

Appendix B

TGA results for orth- and cub-C_3A systems hydrated in water for 4 minutes are shown in Figure B1.

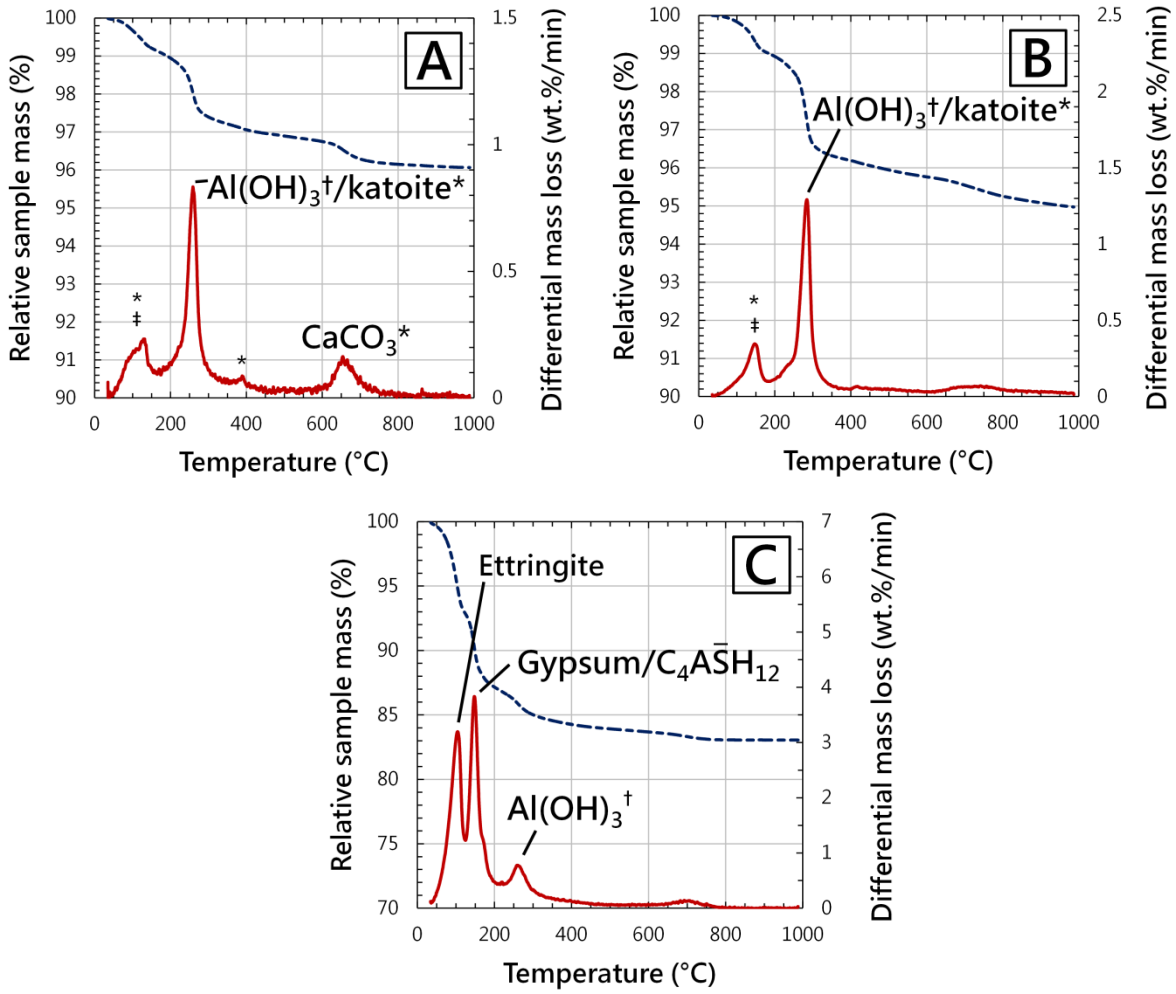

Figure B1. TGA results of (A) orth-C_3A_2 and (B) cub-C_3A_1 hydrated in water for 4 minutes, and (C) orth-C3A_2 and gypsum_2 hydrated in water for 8 minutes. The labels †, ‡ and * indicate that the $Al(OH)_3$ is amorphous by conventional XRD, mass loss from water in poorly crystalline calcium aluminate hydrates, and $C_4A\bar{C}H_{11}$, respectively. Mass loss from a small amount of $C_4A\bar{C}H_{11}$ may also be present in (C). Minute is abbreviated as min.

Appendix C

Thermodynamic properties of the aqueous complexes and solid phases used in GEM-Selektor v.3 software to calculate SI^{eff} and K_{s0} values are shown in Tables C1-C3.

Table C1: Standard partial molal thermodynamic properties of the aqueous complexes used in the thermodynamic modelling calculations. The reference state is unit activity in a hypothetical one molal solution referenced to infinite dilution.

Species	V° (cm^3/mol)	$\Delta_f H°$ (kJ/mol)	$\Delta_f G°$ (kJ/mol)	S° (J/mol.K)	Cp° (J/mol.K)	Reference
$AlSO_4^+$	-6.0	-1422.7	-1250.4	-172.4	-204.0	[1]
$AlSO_4^{2-}$	31.1	-2338.4	-2006.3	-135.5	-268.4	[1]
Al^{3+}	-45.2	-530.6	-483.7	-325.1	-128.7	[2]
AlO^+ (+ H_2O = $Al(OH)_2^+$)	0.3	-713.6	-660.4	-113.0	-125.1	[2]
AlO_2^- (+ $2H_2O$ = $Al(OH)_4^-$)	9.5	-925.6	-827.5	-30.2	-49.0	[2]
$AlOOH^o$ (+ $2H_2O$ = $Al(OH)_3^o$)	13.0	-947.1	-864.3	20.9	-209.2	[2]
$AlOH^{2+}$	-2.7	-767.3	-692.6	-184.9	56.0	[2]
$CaSO_4^0$	4.7	-1448.4	-1310.4	20.9	-104.6	[1,3]
Ca^{2+}	-18.4	-543.1	-552.8	-56.5	-30.9	[2]
$CaOH^+$	5.8	-751.6	-717.0	28.0	6.0	[2]
$NaSO_4^-$	18.6	-1146.7	-1010.3	101.8	-30.1	[1]
Na^+	-1.2	-240.3	-261.9	58.4	38.1	[2]
$NaOH^0$	3.5	-470.1	-418.1	44.8	-13.4	[2]
H_2^0	25.3	-4.0	17.7	57.7	166.9	[4]
N_2^0	33.4	-10.4	18.2	95.8	234.2	[4]
O_2^0	30.5	-12.2	16.4	109.0	234.1	[4]
$S_2O_3^{2-}$	27.6	-649.9	-520.0	66.9	-238.5	[2]
HSO_3^-	33.0	-627.7	-529.1	139.7	-5.4	[2]
SO_3^{2-}	-4.1	-636.9	-487.9	-29.3	-281.0	[2]
HSO_4^-	34.8	-889.2	-755.8	125.5	22.7	[2]
$SO4^{2-}$	12.9	-909.7	-744.5	18.8	-266.1	[2]
H_2S^0	35.0	-39.0	-27.9	125.5	179.2	[4]
HS^-	20.2	-16.2	12.0	68.2	-93.9	[2]
S^{2-}	0	-16.2	120.4	-295.6	-93.9	[1]
OH^-	-4.7	-230.0	-157.3	-10.7	-136.3	[2]
H^+	0	0	0	0	0	[2]
H_2O^0	18.1	-285.9	-237.2	69.9	75.4	[5]

Table C2: Standard partial molar thermodynamic properties of the solid phases used in the thermodynamic modelling calculations. The reference state is 298.15 K and 1 bar.

Phase	V ° (cm^3/mol)	$\Delta_f H°$ (kJ/mol)	$\Delta_f G°$ (kJ/mol)	S° (J/mol.K)	Cp° (J/mol.K)	Reference
Cub-C_3A	89.2	-3560.6	-3382.3	205.4	209.4	[6-8]
Gypsum	74.7	-2023.4	-1797.8	193.8	186.2	[1,9]
Hemihydrate	61.7	-1575.3	-1436.3	134.3	124.1	[10]
C_4AH_{19}	370.1	-10018	-8749.9	1120	1382	[11]
$C_2AH_{7.5}$	179.7	-5277.5	-4695.5	450	535.9	[11]
Katoite	149.7	-5537.3	-5008.2	421.7	445.6	[11]
$C_4A\bar{S}H_{12}$	309.0	-8750	-7778.5	821.0	942.4	[7,12]
Ettringite	707.0	-17535	-15206	1900	2174.4	[7,12]
Portlandite	33.1	-984.7	-897.0	83.4	87.5	[1,9]
½AH_3 (microcrystalline)	32.0	-1265.3	-1148.4	140.0	93.1	[11]

Table C3: Reactions and K_{s0} values of the solid phases used in the thermodynamic modelling calculations.

Phase	Reaction	$\log_{10}(K_{s0})$	Reference
Cub-C_3A	$Ca_3Al_2O_6 + 2H_2O \rightleftharpoons 3Ca^{2+} + 2AlO_2^- + 4OH^-$	15.01*	[6-8]
Gypsum	$CaSO_4{\cdot}2H_2O \rightleftharpoons Ca^{2+} + SO_4^{2-} + 2H_2O$	-4.581	[1,9]
Hemihydrate	$CaSO_4{\cdot}0.5H_2O \rightleftharpoons Ca^{2+} + SO_4^{2-} + 0.5H_2O$	-3.59	[10]
C_4AH_{19}	$Ca_4Al_2(OH)_{14}{\cdot}12H_2O \rightleftharpoons 4Ca^{2+} + 2AlO_2^- + 6OH^- + 16H_2O$	-25.45	[11]
$C_2AH_{7.5}$	$Ca_2Al_2(OH)_{10}{\cdot}2.5H_2O \rightleftharpoons 2Ca^{2+} + 2AlO_2^- + 2OH^- + 2H_2O$	-13.80	[11]
Katoite	$Ca_3Al_2(OH)_{12} \rightleftharpoons 3Ca^{2+} + 2AlO_2^- + 4OH^- + 2H_2O$	-20.50	[11]
$C_4A\bar{S}H_{12}$	$Ca_4Al_2(SO_4)(OH)_{12}{\cdot}6H_2O \rightleftharpoons 4Ca^{2+} + 2AlO_2^- + SO_4^{2-} + 4OH^- + 10H_2O$	-29.26	[7,12]
Ettringite	$Ca_6Al_2(SO_4)_3(OH)_{12}{\cdot}26H_2O \rightleftharpoons 6Ca^{2+} + 2AlO_2^- + 3SO_4^{2-} + 4OH^- + 30H_2O$	-44.9	[7,12]
Portlandite	$Ca(OH)_2 \rightleftharpoons Ca^{2+} + 2OH^-$	-5.20	[1,9]
½AH_3 (microcrystalline)	$Al(OH)_3 + OH^- \rightleftharpoons AlO_2^- + 2H_2O$	-0.67	[11]

* The K_{s0} value for cub-C_3A was calculated here using the referenced data.

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